JC10 Rec'd PCT/PTO 02 JAN 2002

293450°FORM PTO-1390 U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE
(REV 11-2000)

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. § 371

ATTORNEY'S DOCKET NUMBER	U.S. APPLICATION NO. (If known, see 37 CFR 1.5)
300602002400	10/019666 to be assigned

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/KR00/00984	30 August 2000	3 May 2000

TITLE OF INVENTION
LOW TEMPERATURE SINTERABLE AND LOW LOSS DIELECTRIC CERAMIC COMPOSITIONS AND METHOD THEREOF

APPLICANT(S) FOR DO/EOUnited States
Yoon-Ho KIM and Hyo-Tae KIM

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [x] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. [ ] This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. [ ] The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).
5. [x] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. [x] is attached hereto (required only if not communicated by the International Bureau).
   b. [ ] has been communicated by the International Bureau.
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [ ] An English language translation of the International Application under PCT Article 19 (35 U.S.C. 371(c)(2)).
   a. [ ] is attached hereto.
   b. [ ] has been previously submitted under 35 U.S.C. 154(d)(4).
7. [ ] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
   a. [ ] are attached hereto (required only if not communicated by the International Bureau).
   b. [ ] have been communicated by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [ ] have not been made and will not be made.
8. [ ] An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. [ ] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [ ] An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. [ ] An Information Disclosure Statement under 37 CFR 1.97 and 1.98 and Form PTO 1449 (copies of references to be provided)
12. [ ] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [ ] A FIRST preliminary amendment.
14. [ ] A SECOND or SUBSEQUENT preliminary amendment.
15. [ ] A substitute specification.
16 [ ] A change of power of attorney and/or address letter.
17 [ ] A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18 [ ] A second copy of the published international application under 35 U.S.C. 154(d)(4).
19 [ ] A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. [x] Other items or information: PCT/IB/301, PCT/IB/304, PCT/IB/308, and Application Data Sheet

CERTIFICATE OF HAND DELIVERY

I hereby certify that this correspondence is being hand filed with the United States Patent and Trademark Office in Washington, D.C. on January 2, 2002.

N Slaveter
N. Slaveter

531 Rec'd PCT/PTC 02 JAN 2002

U.S. APPLICATION NO. (if known, see 37 CFR 1.5) to be assigned 10/019666	INTERNATIONAL APPLICATION NO. PCT/KR00/00984	ATTORNEY DOCKET NUMBER: 300602002400

21. ☒ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO..........................$1,040.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO......................$890.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO............................$740.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provision of PCT Article 33(1)-(4) $710.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) $100.00

CALCULATIONS PTO USE ONLY

				CALCULATIONS	PTO USE ONLY
ENTER APPROPRIATE BASIC FEE AMOUNT =				$890.00	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	7 - 20 =	--	x $18.00	$--	
Independent claims	4 - 3 =	1	x $84.00	$84.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ $280.00	$	
TOTAL OF ABOVE CALCULATIONS =				$974.00	
☒ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by ½.				$--	
SUBTOTAL =				$487.00	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$	
TOTAL NATIONAL FEE =				$	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00 per property** +				$	
TOTAL FEES ENCLOSED =				$487.00	
				Amount to be refunded:	**$**
				charged:	**$487.00**

a. ☐ A check in the amount of $ to cover the above fees is enclosed.

b. ☒ Please charge my **Deposit Account No. 03-1952** in the amount of **$487.00** to cover the above fees. A duplicate copy of this sheet is enclosed. Please reference Docket No. 30060.20024.00 .

c. ☒ The Commissioner is hereby authorized to charge any additional fees that may be required, or credit any overpayment to **Deposit Account No. 03-1952**. A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Raj S. Davé, Ph.D.
Morrison & Foerster LLP
2000 Pennsylvania Avenue, N.W.
Washington, D.C. 20006-1888

January 2, 2002

SIGNATURE

Raj S. Davé, Ph.D.
Registration No. 42,465

1 /PRTS

10/019666

PCT/KR00/00984

531 Rec'd PCT/PTO 02 JAN 2002

LOW TEMPERATURE SINTERABLE AND LOW LOSS DIELECTRIC CERAMIC COMPOSITIONS AND METHOD THEREOF

TECHNICAL FIELD

The present invention relates to a low temperature sinterable and low loss dielectric ceramic compositions for use in fabricating various high frequency devices such as a multilayer chip capacitor, a multilayer chip filter, a multilayer chip capacitor inductor composite device and module, a low temperature sinterable substrate, a resonator or a filter and a ceramic antenna, and its method.

BACKGROUND ART

Recently, with the rapid development in a mobile communication and a satellite communication, a high frequency dielectric ceramics is in a high demand as a material for a high frequency integrated circuit or a dielectric resonator.

Major characteristics of the dielectric ceramics used for a high frequency includes a high dielectric constant (ε_r), a quality factor (Q) and a stable and tunable temperature coefficient (τ_f) of a resonance frequency.

Representative high frequency dielectric compositions which have been widely known up to now are (Zr, Sn)TiO_4 group, BaO-TiO_2 group, (Mg, Ca)TiO_3 group, and Ba-$(Zn_{1/3}Ta_{2/3})O_3$, $Ba(Mg_{1/3}Ta_{2/3})O_3$, $Ba(Zn_{1/3}Nb_{2/3})O_3$ as Ba-peropskite group etc.

However, these compositions are disadvantages in that they are mostly

fired at a high temperature of 1,300~1,500°C, phase synthesis is not easy, a dielectric constant is low or a high-priced material should be used.

Besides, lately, advancement of a portable information communication devices lead to development of various types of substrates and multi-chip module (MCM) by a multilayer chip high frequency devices or low temperature co-firing ceramics (LTCC), and a research and development of a low temperature firing high performance high frequency ceramics are conducted accordingly.

However, there are problems that the performance of the high frequency characteristic is considerably degraded such as, for example, most of them are not sufficient in terms of density when being fired at a low temperature, a dielectric constant is decreased according to addition of a sintering aid, a quality factor is degraded and a temperature factor is changed.

In addition, silver or copper conduct with a small high frequency loss and a cofiring available low temperature firing high frequency dielectric ceramic are very rare.

Therefore, an object of the present invention is to provide a dielectric ceramics composition which can be fired at a very low temperature but has an excellent high frequency dielectric characteristic of various temperature compensation characteristics according to a high quality factor, a dielectric constant, a stable temperature factor and a composition, and can be implemented at a low cost.

Another object of the present invention is to provide a dielectric ceramics

composition which can employ Ag, Cu, their alloy or a Ag/Pd alloy as an internal electrode and thus be used for various high frequency devices, such as a multilayer chip capacitor, a multilayer chip filter, a multilayer chip capacitor/inductor composite device and a low temperature sinterable substrate, a resonator and a filter or a ceramic antenna.

DETAILED DESCRIPTION OF THE INVENTION

In order to achieve the above objects, there is provided a dielectric ceramics composition which is constructed by combining 1 mole of $(Zn_{1-x}M_x)TiO_3$ and $yTiO_2(0 \le y \le 0.6$ as a main component, one of 0~5 wt % B_2O_3, 0~5 wt % H_3BO_3, 0~5 wt % SiO_2-K_2O glass, 0~5 wt % B_2O_3 and SiO_2-K_2O glass, or 0~5 wt % H_3BO_3 and SiO_2-K_2O glass is added as an additive thereto, and fired at a low temperature of 800~925°C, its preparation method, and a high frequency dielectric ceramics device using the same. In this respect, 'M' is one of Mg, Co, Ni, 'x' is $0 \le x \le 0.55$ in case of Mg and 'x' is $0 \le x \le 1$ in case of Co, and $0 \le x \le 1$ in case of Ni

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing a phase dissociation temperature of $(Zn_{1-x}M_x)TiO_3$ according to the substituted amount of Mg.

MODE FOR CARRYING OUT THE PREFERRED EMBODIMENTS

The present invention will now be described with reference to

accompanying drawings.

A high frequency dielectric ceramics composition of the present invention is characterized in that it has a very low firing temperature (800~925°C) compared to that of a conventional dielectric composition, has an excellent high frequency dielectric characteristic of various temperature compensation characteristics (τf = -52 ~ +104 ppm/°C) according to a high quality factor (Q x f = 12,000 ~ 84,000 GHz), a dielectric constant ($16 \leq \varepsilon r \leq 32$), a stable temperature factor and a composition, and can be implemented with a low-priced material such as ZnO, MgO, CoO, NiO, TiO_2,

In addition, the high frequency dielectric ceramics composition of the present invention is also characterized in that it employs Ag, Cu, their alloy or a Ag/Pd alloy as an internal electrode and thus be used for various high frequency devices, such as a multilayer chip capacitor, a multilayer chip filter, a multilayer chip capacitor/inductor composite device and a low temperature firing substrate, a resonator and a filter or a ceramic antenna.

In the present invention, the low temperature firing composition of the present invention has an excellent quality factor (close to the existing high temperature firing composition) more than several times the existing one. In addition, in the claimed composition coverage, combination of composition having an excellent high frequency characteristic of the almost infinite number can be obtained compared to any of the conventional ones.

$ZnTiO_3$ (crystal structure has a rhombohedral symmetry) is phase-dissociated to Zn_2TiO_4 (cubic symmetry) and TiO_2 (rutile) at a higher

temperature than 945°C (refer to Fig.303 of Phase Diagrams for Ceramist by the American Ceramic Society, System $ZnO-TiO_2$ by Dulin and Rase), and thus, it is very difficult to be prepared.

In order to obtain a pure $ZnTiO_3$, phase synthesis and firing must be made at a below 945°C. A preliminary experiment of the present invention shows a result through an X-ray diffraction analysis that phase dissociation starts at near 925°C so that a thermal treatment must be performed at below 925°C.

In a preferred embodiment of the present invention, in order to remove the shortcomings, Zn^{2+}, a positive ion of A-site constituting an ABO_3 type ilmenite phase ceramics, is substituted with Mg^{2+} (up to 0.55 mole), to thereby enlarge a thermal stabilization temperature of $ZnTiO_3$ to a high temperature range (refer to Figure 1), so that the preparation process coverage is widened and the high frequency dielectric characteristic are highly improved.

Figure 1 is a graph showing a phase dissociation temperature of $(Zn_{1-x} Mg_x)TiO_3$ according to the substituted amount of Mg. In case that a region x = 0, $ZnTiO_3$ is dissociated at a temperature of 945°C, and since the dissociation temperature goes up to a high temperature by the substitution of Mg, a single phase of the $(Zn_{1-x} Mg_x)TiO_3$ solid solution can be synthesized or fired even at a temperature of higher than 945°C.

Accordingly, a single phase can be obtained anywhere in the region II of Figure 1, which is the phase synthesis region of the present invention.

A high frequency dielectric ceramics composition in accordance with a

preferred embodiment of the present invention will now be described.

Powders (an average particle diameter is 1μm) of ZnO, MO (in this respect, MO is MgO, CoO or NiO) and TiO_2 (>99%) was weighed according to a composition range of $(Zn_{1-x}M_x)TiO_3$ and $yTiO_2$ (M is one of Mg, Co and Ni, x is $0 \leq x \leq 0.55$ in case of Mg, x is $0 \leq x \leq 1$ in case of Co, x is $0 \leq x \leq 1$ in case of Ni, and y is $0 \leq y \leq 0.6$), mixed in a wet ball mill method, dried at 120°C, and calcined and synthesized at a temperature of 850~950°C for four hours.

The calcined powder was mixed with 0.5 wt % B_2O_3, 0~5 wt % SiO_2-K_2O glass and a combination of 0~10 wt % B_2O_3 and SiO_2-K_2O as a sintering aid.

At this time, in case of B_2O_3, besides the oxide, a water soluble boron (H_3BO_3) was used to improve homogeneity in adding a little amount.

Solubility (per water 100cc) of boron to cool water (30°C) and hot water (100°C) is 6.35 and 27.6 (refer to Handbook of Chemistry and Physics, 55th ed., CRC Press, 1974-75).

In case of the present invention, cool water was used to make boron corresponding to the solubility to an aqueous solution, into which the main component or the main composition and the glass powder are mixed and crushed.

In crushing, since the temperature of slurry goes up further (especially, up to 45°C in case of high speed centrifugal crushing), the mixture of boron can be more uniform.

As for the SiO_2-K_2O glass, SiO_2 and K_2CO_3 were mixed with K_2CO_3 by 55~75 wt % and 25~45 wt %, melt at a temperature of 1100~1200°C, quenched

at cool deionized water, ball-milled for 24 hours, thereby obtaining glass powder, and it was confirmed that an amorphous phase of glass was obtained according to an X-ray diffraction analysis result.

Since the present invention is aimed at a low temperature firing at a below 925°C, in order to obtain fine powder (average particle diameter of below 0.5μm) less than submicron, a stabilized zirconia ball with a diameter of 2mm was used and crushed for four hours by an attrition mill, or a fine stabilized zirconia ball with a diameter of 1mm was used and subjected to a high speed centrifugal crushing for 5~10 minutes.

An aqueous solution to which 2 wt % PVA binder was added is mixed with the dried powder to make a granule of about 150μm and shaped to a disk test sample having a diameter of 8mm and a thickness of 3.8mm at a pressure of 98 Mpa.

The shaped test sample was maintained at a temperature of 300~500°C for over 3 hours to burn out the binder, and then sintered at a temperature 800~925°C at an atmosphere.

At this time, a heating rate was 10°C/min. The sintered test sample was ground with an SiC polishing paper (#1,500) to obtain about 0.45 ratio of diameter to thickness of the test sample.

The high frequency dielectric characteristic was measured in a $TE_{01\delta}$ mode by using a network analyzer (HP 8720C) by making a cylindrical dielectric ceramics resonator, and a dielectric constant was measure by a Hakki-Coleman method, a quality factor was measure by an open cavity method, a

temperature factor of a resonance frequency was measured by an invar cavity at a temperature range of +20~+70°C.

Table 1 shows a high frequency dielectric characteristic in case that B_2O_3, boron (H3BO3) and a combination component of boron and SiO_2-K_2O glass are added as sintering aids to a main composition that x=0.01 and y=0I2 among $(Zn_{1-x}M_x)TiO_3$ $(0 \le x \le 0.55)$ and $yTiO_2$ $0 \le y \le 0.6)$ composition.

In Table 1, a 800°C-sintered body had about more than 92% relative density, and 875°C-sintered body had about more than 97% relative density.

In the embodiments 2~5 and 6~10, it is noted that quality factor was further improved in case of adding boron instead of adding B_2O_3, and as for the temperature coefficient, the variation rate according to the sintering temperature (800°C and 875°C) was smaller. This effect results from a uniformity of boron.

As the sintering characteristic thanks to addition of B_2O_3, the dielectric constant and quality factor were much increased, and were increased up to about 2 wt % and then reduced at 5 wt %.

The temperature coefficient was moved to a positive as the amount of B_2O_3 is increased.

Accordingly, in the embodiments of Table 1, it is anticipated that if the value 'y' is a bit increased more than 0.2 and the amount of additive is controlled, an excellent dielectric property of which the temperature factor is almost '0' can be obtained.

That is, in order to be a usable high frequency characteristic, not only TiO_2, but the amount of additive needs to be controlled property, and

accordingly, various composition groups can be obtained.

Table 1: High frequency dielectric property of a dielectric resonator fabricated with composition of $(Zn_{00.99}M_{0.01})TiO_3$ (M=Mg) + $0.2TiO_2$ + (B_2O_3, H_3BO_3, or H_3BO_3 + SiO_2-K_2O glass)

No.	B_2O_3 (wt%)	H_2BO_3 (wt%)	SiO_2-K_2O glass (wt%)	Sintering temperature (°C)	Dielectric constant (ε_r)	Quality factor (Qxf GHz)	Temperature coefficient (τf:ppm/°C)
1	-	-	-	800	13.8	22900	-22
				875	21.1	32400	-50
2	0.25	-	-	800	22.3	65700	-52
				875	26.9	78200	-48
3	0.50	-	-	800	23.0	54800	-43
				875	26.4	84600	-40
4	1.00	-	-	800	19.7	50100	-44
				875	26.5	80900	-33
5	2.00	-	-	800	19.6	44800	-29
				875	27.2	79300	-22
6	-	0.25	-	800	22.1	59800	-46
				875	27.0	84300	-43
7	-	0.50	-	800	20.2	50600	-44
				875	26.0	85200	-39

8	-	1.00	-	800	19.3	47700	-33
				875	26.3	81200	-34
9	-	2.00	-	800	19.5	45400	-40
				875	26.7	70100	-20
10	-	5.00	-	800	16.5	40000	-10
				875	25.1	60200	+20
11	-	0.50	0.50	800	19.5	58800	-43
				875	25.8	67200	+39
12	-	0.50	1.00	800	17.0	42400	-20
				875	23.6	58400	-38
13	-	0.50	2.00	800	16.7	26300	-17
				875	23.8	45100	-36
14	-	0.50	3.00	800	15.4	25000	-21
				875	24.1	36200	-29
15	-	0.50	5.00	800	13.7	19100	-19
				875	23.4	24500	-43

Table 2 indicates a dielectric property in case of increasing the amount of Mg and TiO_2 (x = 0.55, Y = 0.6).

Table 2: High frequency dielectric property of a dielectric resonator fabricated with a composition of $(Zn0_{0.45}M_{0.55})TiO_3$ (M=Mg) + $0.6TiO_2$ + (B_2O_3, H_3BO_3, or H_3BO_3 + SiO_2-K_2O glass)

No.	B_2O_3 (wt%)	H_2BO_3 (wt%)	SiO_2-K_2O glass (wt%)	Sintering temperature (°C)	Dielectric constant (ε_r)	Quality factor (Qxf GHz)	Temperature coefficient (τf:ppm/°C)
16	-	-	-	900	20.2	18300	+60
				925	24.3	20700	+56
17	0.25	-	-	900	26.9	19700	+54
				925	30.1	35300	+78
18	0.50	-	-	900	26.9	20300	+57
				925	29.5	44000	+65
19	1.00	-	-	900	26.0	22300	+51
				925	28.4	35300	+87
20	2.00	-	-	900	25.7	22400	+57
				925	28.6	30500	+79
21	-	0.25	-	900	27.3	23200	+72
				925	30.1	58900	+86
22	-	0.50	-	900	26.5	23000	+72
				925	29.3	46000	+70
23	-	1.00	-	900	25.3	23100	+55
				925	28.2	33400	+73
24	-	2.00	-	900	25.5	21700	+68
				925	28.1	27300	+88
25	-	5.00	-	900	23.7	21200	+75

				925	27.5	16600	+104
26	-	0.50	0.50	900	22.8	27900	+54
				925	26.8	22700	+79
27	-	0.50	1.00	900	24.2	29800	+46
				925	29.0	26800	+76
28	-	0.50	2.00	900	28.4	22300	+65
				925	32.0	17900	+71
29	-	0.50	3.00	900	28.9	27600	+49
				925	32.5	19500	+84
30	-	0.50	5.00	900		21200	+33
				925		11900	+53

In the above embodiments, positive temperature coefficients were obtained. In this case, a temperature coefficient of '0' can be naturally obtained by adequately reducing the amount of TiO_2.

Meanwhile, in case that $x > 0.55$, the dielectric constant and the quality factor were much degraded than those of the present invention, and most of all, the sintering characteristic is degraded as the amount of Mg is increased.

Table 3 indicates a composition exhibiting an excellent dielectric property with a temperature coefficient of '0' on the basis of Table 1 and Table 2.

Table 3: High frequency dielectric property of a dielectric resonator fabricated with a composition of $(Zn0_{0.70}M_{0.30})TiO_3$ (M=Mg) + $0.2TiO_2$ + (B_2O_3, + SiO_2-K_2O glass)

No.	B_2O_3 (wt%)	SiO_2-K_2O glass (wt%)	Sintering temperat-ure (°C)	Dielectric constant (ε_r)	Quality factor (Qxf GHz)	Temperature coefficient (τf:ppm/°C)
31	-	0.50	925	16.6	26900	-16
32	0.25			24.5	65300	-11
33	0.50			24.9	69700	-6
34	1.00			24.7	74700	-10
35	1.50			24.4	69000	-1
36	2.00			24.2	67300	-5
37	-	1.00	925	17.1	27200	-27
38	0.25			24.8	58500	-14
39	0.50			25.0	59200	-7
40	1.00			25.0	59300	-2
41	1.59			24.7	55400	0
42	2.00			24.5	55800	+1
43	-	2.00	925	18.3	20300	-14
44	0.25			25.1	52200	-9
45	0.50			25.2	52700	-4
46	1.00			25.0	55700	+5
47	1.50			25.3	48100	+2
48	2.00			24.9	50800	+14

No.	B_2O_3 (wt%)	SiO_2-K_2O glass (wt%)	Sintering temperat-ure (°C)	Dielectric constant (ε_r)	Quality factor (Qxf GHz)	Temperature coefficient (τf:ppm/°C)
49	-	3.00	900	17.6	25400	-24
50	0.25			21.9	33600	-20
51	0.50			23.8	39100	-10
52	1.00			25.6	38400	+17
53	1.50			25.6	44800	+20
54	2.00			25.5	42100	+26
55	-	5.00	900	19.5	19500	-17
56	0.25			21.8	27100	-20
57	0.50			22.8	30700	-32
58	1.00			23.9	31600	-11
59	1.50			25.0	36800	+24
60	2.00			25.1	37700	+31

In the embodiments 32~60, an excellent dielectric property with a dielectric constant of more than 24, a quality factor of more than 50000 and a temperature factor of ± 30ppm/°C was obtained from the combination of less than 2 wt % B_2O_3 (or H_3BO_3) and SiO_2-K_2O glass.

Table 4 shows an influence of B2O3 and H3BO3 additive for the composition of $(Zn_{0.70}Mg_{0.30})TiO_3$ and $0.2TiO_2$.

Table 4: High frequency dielectric property of a dielectric resonator fabricated with a composition of $(Zn0_{0.70}M_{0.30})TiO_3$ (M=Mg) + $0.2TiO_2$ + (B_2O_3, or H_3BO_3)

No.	B_2O_3 (wt%)	H_2BO_3 (wt%)	Sintering temperat-ure (°C)	Dielectric constant (ε_r)	Quality factor (Qxf GHz)	Temperature coefficient (τf:ppm/°C)
61	-	-	900	19.3	51200	-31
			925	22.5	84400	-29
62	0.25	-	900	23.6	50000	-23
			925	25.7	86100	-16
63	0.50	-	900	22.8	44000	-23
			925	25.5	77400	-13
64	1.00	-	900	22.4	46300	-15
			925	25.2	78000	+1
65	2.00	-	900	23.1	56600	0
			925	25.8	87600	-1
66	-	0.25	900	23.5	52000	-16
			925	25.3	84300	-15
67	-	0.50	900	23.6	46200	-6
			925	25.3	81700	-7
68	-	1.00	900	23.6	53700	-10
			925	25.2	79300	-5

69	-	2.00	900 925	24.5 26.1	56600 77200	-12 -7
70	-	5.00	900 925	16.5 25.1	40000 60200	-4 -4

In the embodiments 62~65 and 66~69, it is noted that the dielectric constant and the quality factor were higher when H3BO3 were added than B2O3, and especially, the stability of the temperature factor according to the sintering temperature was excellent, which testifies the effect of the present invention.

In the present invention, a high frequency dielectric ceramics composition may be constituted by combining a combination of $(Zn_{1-a}Mg_{1-b}Co_{1-c}Ni_{1-d})TiO_3$ and $yTiO_2$ as a main component and one of 0~5 wt % B_2O_3, 0~5 wt % H_3BO_3, 0~5 wt % SiO_2-K_2O glass, 0~5 wt % B_2O_3 and SiO_2-K_2O glass, or 0~5 wt % H_3BO_3 and SiO_2-K_2O glass as an additive, which satisfies conditions of $0 \le a \le 1$, $0 \le b \le 1$, $0 \le c \le 1$, $0 \le d \le 1$ and $0 \le y \le 0.6$.

INDUSTRIAL APPLICABILITY

As so far described, a high frequency dielectric characteristic having an excellent various temperature compensation varied according to the high quality factor, the dielectric constant and the stable temperature coefficient and composition but having a very low sintering temperature compared with the conventional dielectric composition can be implemented at a low-priced

material such as ZnO, MgO, CoO, NiO or TiO_2.

In addition, since Ag, Cu or their alloy or Ag/Pd alloy can be used as an internal electrode, and thus, can be used as various high frequency devices, i.e., a multilayer chip capacitor, a multilayer chip filter, a multilayer chip capacitor/inductor composite device and a low-temperature sinterable substrate, a resonator and a filter or a ceramic antenna.

Especially, the low-temperature sintered composition obtains a remarkably high quality factor more than several times that of the conventional one.

In addition, combination of the almost infinite number of compositions exhibiting the excellent high frequency characteristic can be obtained in the composition range of the present invention.

CLAIMS

1. A high frequency dielectric ceramics composition constituted by combining a combination of $(Zn_{1-x}M_x)TiO_3$ and $yTiO_2$ as a main component, into which one of 0~5 wt % B_2O_3, 0~5 wt % H_3BO_3, 0~5 wt % SiO_2-K_2O glass, 0~5 wt % B_2O_3 and SiO_2-K_2O glass, or 0~5 wt % H_3BO_3 and SiO_2-K_2O glass is added as an additive, satisfies conditions of

M is Mg, Co or Ni,

'x' is $0 \leq x \leq 0.55$ in case of Mg and 'x' is $0 \leq x \leq 1.0$ in case of Co, and $0 \leq x \leq 1.0$ in case of Ni, and

$0 \leq y \leq 0.6$.

2. A high frequency dielectric ceramics composition preparation method in which material powder of ZnO, MO (in this respect, MO is MgO, CoO or NiO) and TiO_2 is weighed according to a composition range of $(Zn_{1-x}M_x)TiO_3$ and $yTiO_2$ (M is one of Mg, Co and Ni, x is $0 \leq x \leq 0.55$ in case of Mg, x is $0 \leq x \leq 1$ in case of Co, x is $0 \leq x \leq 1$ in case of Ni, and y is $0 \leq y \leq 0.6$), mixed and dried,

the dried powder is calcined at a temperature of 850~950°C,

the calcined powder is mixed with one of 0~5 wt % B_2O_3, 0~5 wt % H_3BO_3, 0~5 wt % SiO_2-K_2O glass, 0~5 wt % B_2O_3 and SiO_2-K_2O glass, or 0~5 wt % H_3BO_3 and SiO_2-K_2O glass as an additive,

the mixed powder is crushed,

the crushed power is shaped,

the shaped body is fired at a temperature of 800~925°C, and

$(Zn_{1-x}M_x)TiO_3$ is calcined at a temperature corresponding to a region (region II) of below a phase dissociation temperature as shown in Figure 1 to obtain $(Zn_{1-x}M_x)TiO_3$ (M is Mg, Co or Ni) of a single phase of rhombohedral/hexagonal crystal.

3. The method of claim 2, wherein the shaped body is made in a manner that an aqueous solution adding a PVA binder is sprayed onto the crushed powder to make a granule, to which a pressure is applied.

4. The method of claim 3, further comprises a step for maintaining the shaped body at a temperature of 300~500°C for a predetermined time and removing the binder.

5. The method of claim 2, wherein $(Zn_{1-x}M_x)TiO_3$ is first calcined, and the calcined $(Zn_{1-x}M_x)TiO_3$ is mixed with one of 0~5 wt % B_2O_3, 0~5 wt % H_3BO_3, 0~5 wt % SiO_2-K_2O glass, 0~5 wt % B_2O_3 and SiO_2-K_2O glass, or 0~5 wt % H_3BO_3 and SiO_2-K_2O glass as an additive, and then fired.

6. A high frequency dielectric ceramics composition constituted by combining a combination $(Zn_{1-a}Mg_{1-b}Co_{1-c}Ni_{1-d})TiO_3$ and $yTiO_2$ as a main component, into which one of 0~5 wt % B_2O_3, 0~5 wt % H_3BO_3, 0~5 wt % SiO_2-K_2O glass, 0~5 wt % B_2O_3 and SiO_2-K_2O glass, or 0~5 wt % H_3BO_3 and SiO_2-

K_2O glass is added as an additive, satisfies conditions of

$0 \le a \le 1$, $0 \le b \le 1$, $0 \le c \le 1$, $0 \le d \le 1$ and

$0 \le y \le 0.6$.

7. Various high frequency devices such as a multilayer chip capacitor, a multilayer chip filter, a multilayer chip capacitor/inductor composite device and a module, a low-temperature sintered substrate, a resonator and a filter or a ceramic antenna, are fabricated by using the dielectric composition of claim 1.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
8 November 2001 (08.11.2001)

PCT

(10) International Publication Number
WO 01/83395 A1

(51) International Patent Classification[7]: C04B 35/46, H01B 3/12

(21) International Application Number: PCT/KR00/00984

(22) International Filing Date: 30 August 2000 (30.08.2000)

(25) Filing Language: Korean

(26) Publication Language: English

(30) Priority Data:
2000-23676 3 May 2000 (03.05.2000) KR

(71) Applicant (*for all designated States except US*): **KOREA INSTITUTE OF SCIENCE AND TECHNOLOGY** [KR/KR]; 39-1, Hawolgok-dong, Sungbook-ku, Seoul 136-791 (KR).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): **KIM, Yoon-Ho** [KR/KR]; Taeneung-woosung Apt. 6-803, Kongneung 2-dong, Nowon-ku, Seoul 139-242 (KR). **KIM, Hyo-Tae** [KR/KR]; Kist Dormitory 36, 39-1, Hawolgok-dong, Sungbook-ku, Seoul 136-791 (KR).

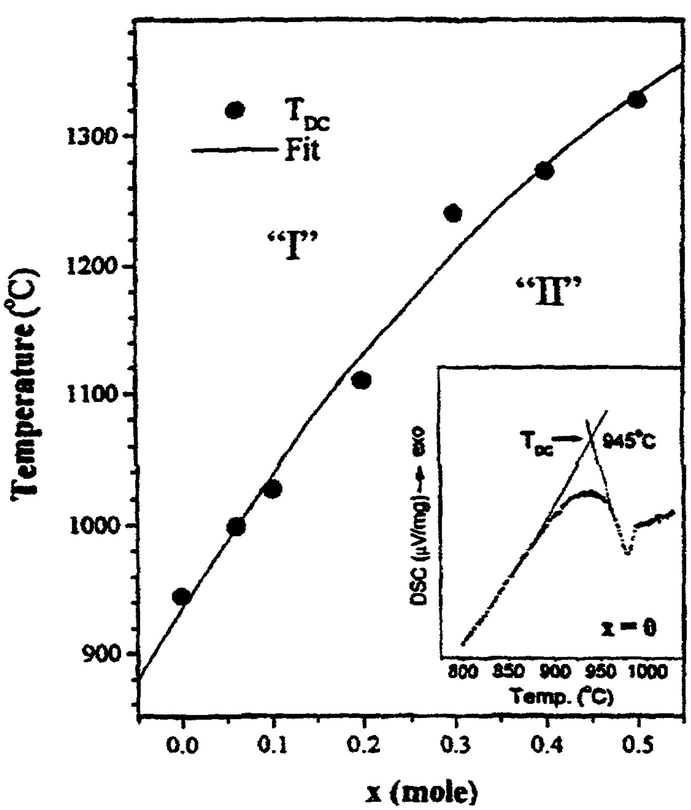
(74) Agent: **PARK, Jang-Won**; Jewoo Building 5th floor, 200, Nonhyun-dong, Kangnam-ku, Seoul 135-010 (KR).

(81) Designated States (*national*): CN, IN, JP, US.

(84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published:
— *with international search report*

(54) Title: LOW TEMPERATURE SINTERABLE AND LOW LOSS DIELECTRIC CERAMIC COMPOSITIONS AND METHOD THEREOF

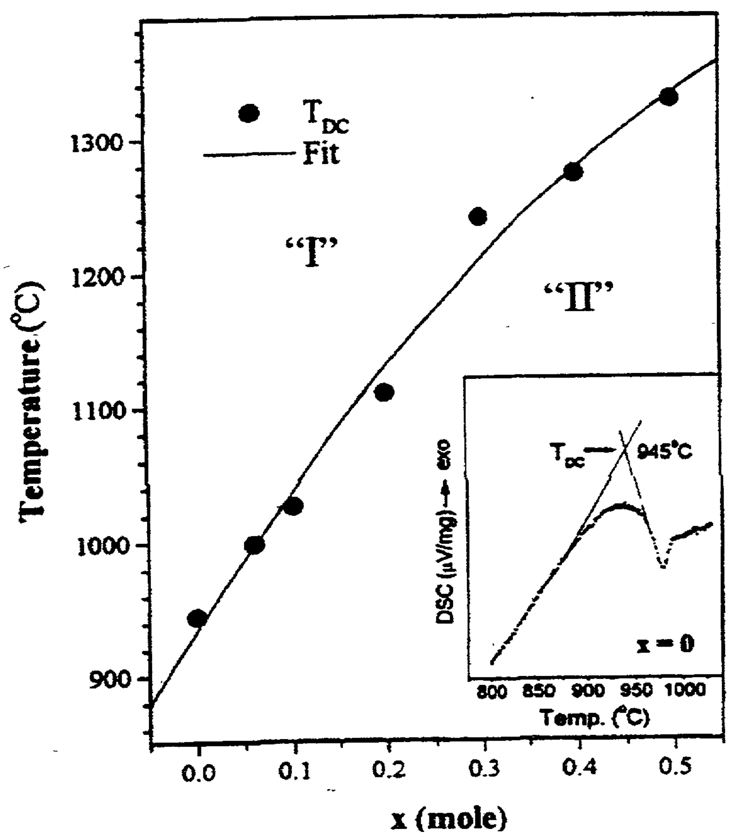


(57) Abstract: A low loss high-frequency dielectric ceramic composition for sintering at a low temperature and method of manufacturing the same which is characterized in that excellent dielectric properties such as a much lower sintering temperature and higher quality coefficient and dielectric constant, compared to a conventional high-frequency ceramic composition, a stabilized temperature coefficient, and a temperature compensating property varied according to a composition, are implemented using a low-priced material such as ZnO-Mo (M=Mg, Co, Ni)-TiO_2. In addition, Ag, Cu, an alloy thereof, or an Ag/Pd alloy can be used as an internal electrode. Thus, the composition of the present invention can be used as a dielectric material for all sorts of high-frequency devices, such as a multilayer chip capacitor, multilayer chip filter, multilayer chip capacitor/inductor composite device and module, low temperature sintered substrate, resonator or filter and ceramic antenna.

WO 01/83395 A1

1/1

FIG 1


T_{DC}
Fit
"I"
"II"
Temperature (°C)
1300
1200
1100
1000
900
0.0
0.1
0.2
0.3
0.4
0.5
x (mole)
T_{DC}
945°C
DSC (μV/mg) → exo
x = 0
800
850
900
950
1000
Temp. (°C)

PATENT
Docket No. 300602002400
Client Ref. PA/KIST/01898

DECLARATION FOR UTILITY PATENT APPLICATION

AS A BELOW-NAMED INVENTOR, I HEREBY DECLARE THAT:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled: LOW TEMPERATURE SINTERABLE AND LOW LOSS DIELECTRIC CERAMIC COMPOSITIONS AND METHOD THEREOF, the specification of which is attached hereto unless the following box is checked:

☒ was filed on January 2, 2002 as United States Application Serial No. 10/019,666 or PCT International Application No. and was amended on (if applicable).

I HEREBY STATE THAT I HAVE REVIEWED AND UNDERSTAND THE CONTENTS OF THE ABOVE-IDENTIFIED SPECIFICATION, INCLUDING THE CLAIMS, AS AMENDED BY ANY AMENDMENT REFERRED TO ABOVE.

I acknowledge the duty to disclose information which is material to the patentability as defined in 37 C.F.R. § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed:

Application No.	Country	Date of Filing (day/month/year)	Priority Claimed?
2000-23676	Korea	3 May 2000	☒Yes ☐No

I hereby claim benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below:

Application Serial No.	Filing Date

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.	Filing Date	Status
PCT/KR00/00984	30 August 2000	☐Patented ☒Pending ☐Abandoned

I hereby appoint the following attorneys and agents to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

Randolph Ted Apple (Reg No. 36,429)
Laurie A. Axford (Reg No. 35,053)
Joseph Barrera (Reg No. 44,522)
Shantanu Basu (Reg No. 43,318)
Frank P. Becking (Reg No. 42,309)
Jonathan Bockman (Reg No. 45,640)
Barry E. Bretschneider (Reg No. 28,055)
Nicholas Buffinger (Reg No. 39,124)
Mark R. Carter (Reg No. 39,131)
Peng Chen (Reg No. 43,543)
Thomas Chuang (Reg No. 44,616)
Cara M. Coburn (Reg No. 46,631)
Raj S. Davé (Reg No. 42,465)
Karen B. Dow (Reg No. 29,684)
Carolyn A. Favorito (Reg No. 39,183)
Hector Gallegos (Reg No. 40,614)
Debra J. Glaister (Reg No. 33,888)
Johney U. Han (Reg No. 45,565)
Alan S. Hodes (Reg No. 38,185)
Kelvan P. Howard (Reg No. P48,999)
Jill A. Jacobson (Reg No. 40,030)
Madeline I. Johnston (Reg No. 36,174)
Parisa Jorjani (Reg No. 46,813)
Richard C. Kim (Reg No. 40,046)
Lawrence B. Kong (Reg No. P49,043)
Glenn Kubota (Reg No. 44,197
Michael J. Mauriel (Reg No. 44,226)
Philip A. Morin (Reg No. P-45,926)
Mabel Ng (Reg No. P48,922)
Catherine M. Polizzi (Reg No. 40,130)
Debra A. Shetka (Reg No. 33,309)
Rebecca Shortle (Reg No. 47,083)
Stanley H. Thompson (Reg No. 45,160)
Michael R. Ward (Reg No. 38,651)
Todd W. Wight (Reg No. 45,218)
David T. Yang (Reg No. 44,415)
George C. Yu (Reg No. 44,418)
Mehran Arjomand (Reg No. P48,231)
Sanjay S. Bagade (Reg No. 42,280)
Erwin J. Basinski (Reg No. 34,773)
Richard R. Batt (Reg No. 43,485)
Vincent J. Belusko (Reg No. 30,820)
Kimberly A. Bolin (Reg No. 44,546)
Tyler S. Brown (Reg No. 36,465)
A. Randall Camacho (Reg No. 46,595)
Robert K. Cerpa (Reg No. 39,933)
Alex Chartove (Reg No. 31,942)
Thomas E. Ciotti (Reg No. 21,013)
Matthew M. D'Amore (Reg No. 42,457)
Peter Davis (Reg No. 36,119)
Stephen C. Durant (Reg No. 31,506)
David L. Fehrman (Reg No. 28,600)
Thomas George (Reg No. 45,740)
Kenneth R. Glick (Reg No. 28,612)
Douglas G. Hodder (Reg No. 41,840)
Charles D. Holland (Reg No. 35,196)
Peter Hsieh (Reg No. 44,780)
Wayne Jaeschke, Jr. (Reg No. 38,503)
Richard D. Jordan (Reg No. 33,519)
Ararat Kapouytian (Reg No. 40,044)
Cameron A. King (Reg No. 41,897)
Kawai Lau (Reg No. 44,461)
Rimas T. Lukas (Reg No. 46,451)
Gladys H. Monroy (Reg No. 32,430)
Kate H. Murashige (Reg No. 29,959)
Martin M. Noonen (Reg No. 44,264)
Paul J. Riley (Reg No. 38,596)
Terri Shieh-Newton (Reg No. 47,081)
Kevin R. Spivak (Reg No. 43,148)
Thomas L. Treffert (Reg No. P48,279)
E. Thomas Wheelock (Reg No. 28,825)
Frank Wu (Reg No. 41,386)
Peter J. Yim (Reg No. 44,417)
Karen R. Zachow (Reg No. 46,332)

Please direct all communications to:

Raj S. Davé, Ph.D., J.D.
Morrison & Foerster LLP
2000 Pennsylvania Avenue, N.W.
Washington, D.C. 20006-1888

Please direct all telephone calls to Raj S. Davé at (202) 887-8798.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

1-00 Apr. 29, 2002
Date

Name: Yoon-Ho KIM
Residence: Seoul, Korea KRX
Citizenship: Korea
Post Office Address: Taeneung-Woosung Apt. 6-803; Kongneung 2-Dong, Nowon-Ku 139-242 Seoul, Korea

2-00 Apr. 29, 2002
Date

Name: Hyo-Tae KIM
Residence: Seoul, Korea KRX
Citizenship: Korea
Post Office Address: KIST Dormitory 36, 39-1, Hawolgok-Dong, Sungbook-ku; 136-791 Seoul, Korea